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14. ABSTRACT
We report progress in two areas of research on NMR of ceramic liquids: the synthesis and characterization of new materials along La-monazite - alumina/CaO joins, and the 27Al NMR measurement of incoherent Al motions in aluminum-containing ceramic melts. The addition of La-monazite to molten alumina or to molten C12A7 produces an increase in tetrahedral bonding in the liquid, as evidenced bythe change of 27Al chemical shift to higher 4-fold values. The increase is not as strong, however, as that produced by the addition of CaO itself. Rates of incoherent, diffusive motions of Al in molten alumina have been measured by pulsed gradient NMR, from melting to ~ 2550 Centigrade, and found to be very high. They are attributable to bulk motions such as random thermal convection currents, but their origin remains an active area of study.

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LASER HEATED GRADIENT NMR STUDIES OF CERAMIC LIQUIDS
AFOSR F4962-03-1-0346 and NSF DMR01-116361

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Abstract

We report progress in two areas of research on NMR of ceramic liquids: the synthesis and characterization of new materials along La-monazite – alumina/CaO joins, and the ^{27}Al NMR measurement of incoherent Al motions in aluminum-containing ceramic melts. The addition of La-monazite to molten alumina or to molten $C_{12}A_7$ produces an increase in tetrahedral bonding in the liquid, as evidenced bythe change of ^{27}Al chemical shift to higher 4-fold values. The increase is not as strong, however, as that produced by the addition of CaO itself. Rates of incoherent, diffusive motions of Al in molten alumina have been measured by pulsed gradient NMR, from melting to ~ 2550 Centigrade, and found to be very high. They are attributable to bulk motions such as random thermal convection currents, but their origin remains an active area of study.

Research Objective

The objective of this research is to probe the structure and motional properties of ceramic liquids, using the technique of ultra high-temperature Nuclear Magnetic Resonance.

New materials synthesis

During the past year we have pursued synthesis and NMR characterization of melts of ternary systems along the alumina-calcia join (Al_2O_3, $C_{12}A_7$ or CA) plus La-monazite ($LaPO_4$), over broad composition ranges. $C_{12}A_7$ is a stable, essentially eutectic compound with melting point 1360 +/- 5 degrees Centigrade and composition $(CaO)_{12}(Al_2O_3)_7$, while CA is the non-eutectic compound $CaAl_2O_4$, which melts at 1602 °C. Our liquid ceramics NMR spectrometer's maximum temperature, using the CO_2 sample heating laser's full ~ (140 W) output, is approximately 2550 °C for samples with emissivities close to 1.0. This is sufficient to melt a wide range of Al-containing ceramics, in which the NMR line of ^{27}Al is easily seen.[1] Part of the reason for investigating the alumina-calcia-monazite system was our interest in also observing the NMR of ^{31}P in refractory melts This nucleus' NMR signals are clearly visible in solutions and in the solid state at ordinary temperatures, but so far they have eluded our observation in molten ceramic samples, even in pure $AlPO_4$, which has an intense ^{27}Al line. The reason for this is not yet known, but it appears most likely that the NMR line of ^{31}P is very broad even in the

liquid state. The implications of such solid-like behavior in a refractory melt at high temperatures may be significant, indicating for example that these liquids possess a complex phase structure.

Our interest in La-monazite's effects on ceramic melts originally arose in connection with its widespread use in ceramic matrix composites as an interphase material, for coatings in engine turbine blades, etc.[2] Samples with initial La-monazite concentrations from 2 to 85% have been characterized for final composition using the electron microprobe, and for structure by X-ray diffraction. All sample preparation and non-NMR characterization at Arizona State University has been performed by Master's student S. Boucher, under the direction of G.H. Wolf. All NMR data were taken by J. Piwowarczyk, senior research associate. In this effort we have also consulted with W.T. Petuskey, Chemistry and Biochemistry, ASU.

With respect to liquid structure and bonding, Al chemical shifts have been measured in molten samples of pure alumina, alumina-monazite, C12A7-monazite and calcium aluminate-monazite. Most of these samples were produced in-house. Competition between four and five-fold bonding is seen in a chemical shift-labelled ternary composition diagram at the end of this report (figure 1). These findings are in general agreement with those of a recent neutron diffraction study[3] of pure Al_2O_3, and extend the chemical shift behavior observed for the alumina-calcia join to La-monazite containing melts. Precipitation of a recently-investigated Ca-La double phosphate was observed following normal sample quenches in water, in La-rich melts having 50% or more $LaPO_4$. This work has been accepted for publication in the Journal of the European Ceramic Society.

MgO-doped alumina samples have recently been supplied to us by A. Sayir (NASA Glenn) and we are examining the strong, single ^{27}Al NMR line observed in their melts for effects of low-level (200 ppm) magnesia doping of alumina.

Finally, in the area of new materials, although we do not have equipment for synthesizing ultra high-melting diboride compounds at our University we have attempted to observe boron NMR of HfB_2 in samples kindly provided by Dr. Eric Wuchina of U.S. Naval Surface Weapons Research. Our findings are very preliminary, but they indicate that line narrowing due to rapid B motions may occur even in the relatively low temperature range 1200 – 1400 °C. We have been reluctant to heat samples in our ultra-high temperature probe past this range, because of the possibility of chemical reactions occurring between HfB_2 and the probe's custom-machined BN levitator, which is both time-consuming and expensive to replace. After informal inquiries about relative chemical inertness of high-temperature machinable ceramics besides BN, we have concluded that zirconia is a good choice of levitator material. A new probe will need to be constructed for this investigation to continue, since the levitator is not a readily-substituted part of the NMR probe.

Characterization of internal motions in ceramic melts via NMR

In this second thrust area we have continued to investigate motions by applying NMR magnetic field gradients to our aerodynamically levitated samples. Using pulsed field gradients in combination with NMR radio frequency pulse sequences we have attempted to measure motions such as diffusion in liquid alumina, over a range of temperatures from melting to approximately 2550 Celsius.

Specifically, we have conducted pulsed gradient spin echo (PGSE) observations of ^{27}Al signal amplitudes attenuated over more than a decade in intensity by Al motions, in molten samples. This is the first step in our efforts to employ NMR towards measurement of individual-ion Al diffusivity measurements, and it has led to a somewhat surprising finding. To our knowledge, ours are the first attempts at NMR measurements of rates of diffusive or other incoherent motions in ceramic melts, using the Stejskal-Tanner pulsed gradient NMR technique. Very high (~ 1.5 x 10^-7 m^2/s), approximately temperature-independent values of these rates were obtained in alumina, which we judge to be at least an order of magnitude too large for individual-ion Al diffusivities, even at such high temperatures (see figure 2).

Initially, the most likely source of large Al motions in spherical samples melted by CO2 laser irradiation from the top, with levitation gas flowing upwards around the bottom, appears to be thermal convection currents. Surface Marangoni flows would not be visible to a bulk technique like NMR, unless such flows extended considerable distances below the molten surface. After hearing our report of these results at the recent ACerS meeting in Indianapolis, however, R. Weber (Containerless Corp., Evanston, Ill.) suggested that the high rates may indicate the presence of volume convection currents caused by relatively rapid (~1 m/s) flow of the levitating gas past the point of nearest approach to the BN levitator wall, where the clearance is estimated to be around 10 microns. The effect may be compared to water waves maintained by a strong wind (the analogy being especially apt because the viscosity of liquid alumina near its melting point is approximately that of water). In addition, thermal convection currents, if present, will contribute similar bulk internal motions.

Faced with evidence last Fall that application of standard Stejskal-Tanner NMR diffusivity measurement techniques to aerodynamically levitated Al2O3 melts would not directly lead to measurements of individual Al ion diffusivities, but rather to measurement of much faster Al motional rates of bulk mass flows, we adopted a new goal. This was to apply approaches well-known in magnetic resonance imaging, which allow discrimination between bulk mass flows and individual molecule or atom diffusive motions. These require use of specially-shaped, bipolar gradient pulses (See monograph by R. Kimmich.[4]) Such pulses are employed in MRI to deal with problems collectively known as motion artifacts, which arise for in vivo imaging of subjects from blood flows, heart action, etc. Shaped gradient pulses can even be used to image motions, for example bulk thermal convection currents.[5]

Applying this knowledge is now the principal thrust of our current efforts, since we have seen directly that that these convection currents exist. First, the effect of varying the viscosity of the sample upon these motional rates should be significant. In order to

monitor this, we plan to measure diffusivity in molten silica-alumina samples of different compositions, and will shortly begin with a mullite sample recently supplied to us by R. Weber. Second, in order to add shaped-gradient pulse capability we have ordered and received a programmable magnetic field gradient pulse amplifier, from Resonance Research, a supplier of specialized electronics used by our NMR spectrometer manufacturer Varian Associates. This purchase was mainly funded from our AFOSR equipment grant, AFOSR F4962-03-1-0346. To program this amplifier we have also received from Varian software for full control of general multiple-axis gradients involved in magnetic resonance imaging (MRI). This not only provides for the programmed shaping of gradient pulses, but automatically confers a second, perhaps equally significant capability upon the high temperature NMR experiment, namely the ability to perform MRI on our levitated samples.

When the gradient coil-equipped ultra high-temperature NMR probe is fully operational, we should be able to make one-dimensional (single-axis) MRI observations of ^{27}Al, in slices of approximately 0.5 mm thickness along the (vertical) direction of the large DC field. Pulse sequences for incoherent motion measurements (like the above-mentioned Stejskal-Tanner sequence) on individual volume elements of a sample are well known in MRI. These will be developed as needed, in much the same way as we have developed pulse sequences for non-MRI pulsed gradient diffusivity measurements, using both our ultra high and standard variable-temperature diffusion probes. Accomplishing this will literally add another dimension, a single spatial Z axis, to our Al motional rate measurements in melts. The other two spatial dimensions X and Y can be added also, but this will require two additional gradient amplifiers plus gradient coils, and represents a substantial further step that will be taken in the development of ultra high-temperature NMR.

Success in performing this set of experimental measurements should lead to a substantial yield of information about the internal dynamics of aerodynamically levitated molten samples. At least part of this yield will be of interest to workers in materials processing at zero gravity. We realize that we may not completely succeed in discriminating between bulk motions and diffusion as sources of Al motional rates, unless we can devise a means of applying alternative levitation techniques such as acoustical or electrostatic, within a superconducting NMR magnet's room-temperature bore. This is a formidable, as-yet unattempted technical feat, however, so that it appears that we should first investigate aerodynamically levitated molten samples of varying viscosities using shaped gradient pulses. In this way we can learn the actual limitations for NMR with aerodynamic levitation. This is the investigation we are beginning to conduct, for the current funding period of the joint AFOSR-NSF grant DMR01-116361.

Conference and publishing activities

The results reported herein have been presented at four conferences: (a) the joint AFOSR-sponsored Directionally Solidified Eutectic Ceramics Workshop in Paris, May 5-7 2003; (b) the Four Corners (Southwest) sectional meeting of the American Physical Society in Tempe, AZ, October 24-25 2003; (c) the annual American Physical Society

March meeting, in Montreal March 21-26 2004; (d) the 106th annual meeting of the American Ceramic Society in Indianapolis, April 18-21 2004.

For the Paris meeting, two posters were given, entitled:
'A Structural Study of Liquid and Solid Phases of the Alumina-CaO-Monazite System', R.F. Marzke. J.Piwowarczyk, S. Boucher, G.H. Wolf and W.T. Petuskey.
'Diffusivity of Al in Molten Al2O3 Measured by Pulsed Gradient Spin Echo NMR of 27Al', R.F. Marzke, J. Piwowarczyk and G.H. Wolf.
Two papers arose from these posters for submission to the Journal of the European Ceramic Society. Their titles are similar to those of the posters, and they have been accepted and are now in final revision of the manuscripts. (see publications, below).

Also during this funding period, R. Marzke acted as co-chair on the first focused session held at the annual March meeting of the American Physical Society (APS) on the general subject of Ceramics, including structural and electronic materials. The session was organized under the auspices of the large industry-government subgroup of APS known as the Forum for Industrial and Applied Physics. Also acting as co-chairs were L. Madsen and A. Sayir. The bulk of the session's program was actually put together by the Dr. Madsen, while the Dr. Sayir gave one of the two invited talks. Except for technical problems in connection with electronic slide projection, the session was deemed a success, mostly because of the efforts of L. Madsen. A symposium is being planned for next year's APS March meeting in Los Angeles, by the group of speakers at Montreal this year. Five speakers will be invited to deliver 36-minute talks, on a range of current topics.

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Personnel Supported

Robert F. Marzke	Associate Professor, Arizona State University
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Publications

"Melt Structure in the Al_2O_3-CaO-$LaPO_4$ System Studied by Ultra High-Temperature ^{27}Al NMR", R.F. Marzke, J. Piwowarczyk, S. Boucher, B. Takulapalli, G.H. Wolf, P.F. McMillan and W.T. Petuskey, J. Europ. Ceram. Soc., accepted.

"Rotational/Convective Incoherent Motion Rates in Levitated, Molten Al_2O_3 Samples Measured by Pulsed Gradient Spin Echo NMR", R. F. Marzke, J. Piwowarczyk, P.F. McMillan and G.H. Wolf, J. Europ. Ceram. Soc., accepted.

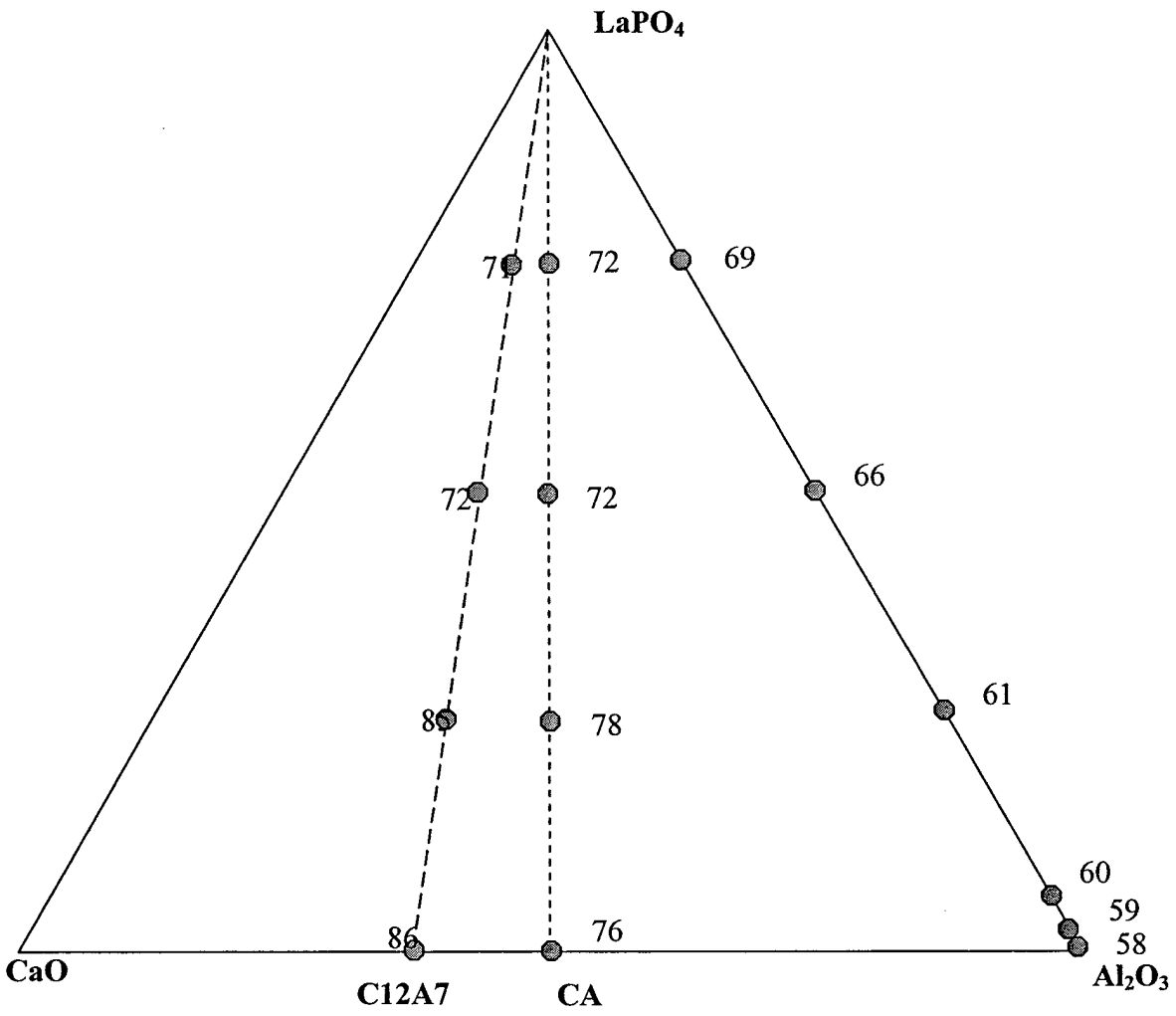

Figure 1. Composition diagram for the Al_2O_3-CaO-$LaPO_4$ system, with ^{27}Al chemical shifts.

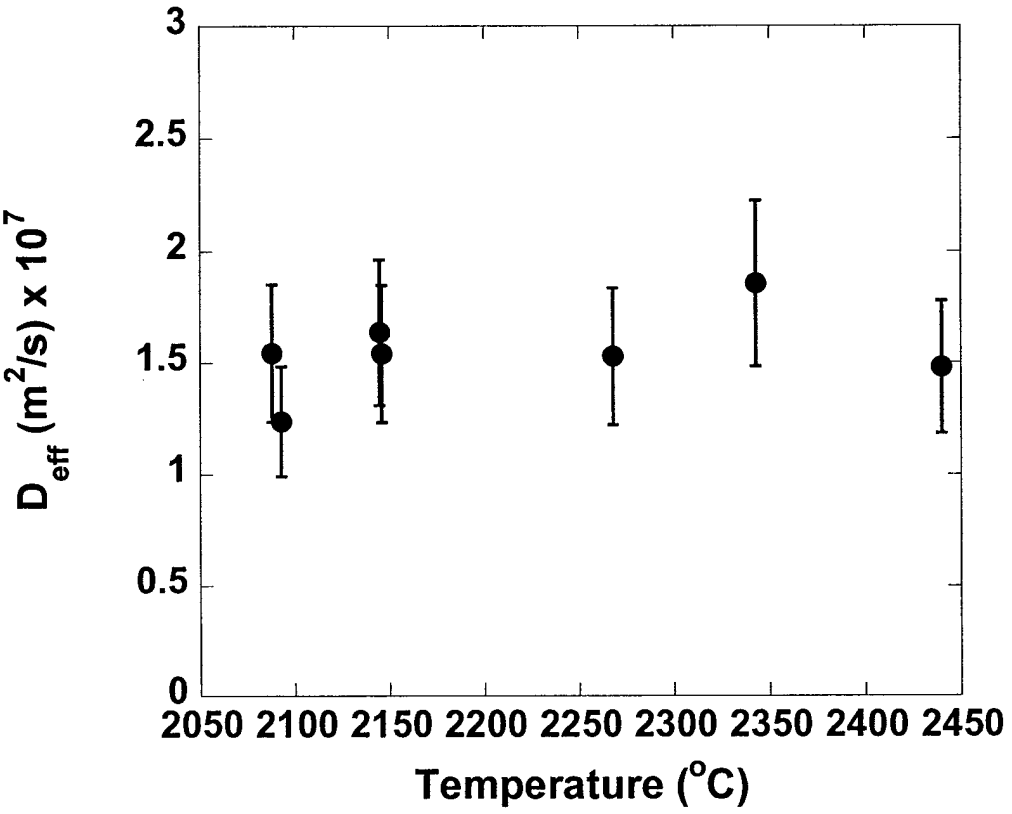

Figure 2. Diffusivity of Al vs. temperature, in molten alumina samples

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